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PREPARATION AND CHARACTERIZATION OF ULTRAPURE POLYSTYRENE SAMPLES

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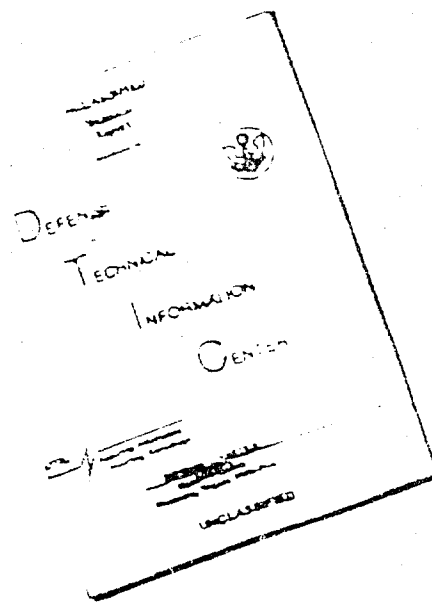
**DIRECTORATE OF MATERIALS AND PROCESSES
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

Project No. 7340, Task No. 734004

(Prepared under Contract No. AF 33(675)-7651;
Mellon Institute, Pittsburgh, Pennsylvania;
Donald P. Wyman and Thomas G Fox, authors)

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FOREWORD

This report was prepared by the Mellon Institute, Pittsburgh, Pa., on Air Force Contract No. AF 33(657)-7651 under Task No. 734004, "New Organic and Inorganic Polymers," of Project No. 7340, "Non-Metallic and Composite Materials." The contract efforts were accomplished under the cognizance of the Nonmetallic Laboratory, Directorate of Materials and Processes, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. The technical work was directed by Lt. Elwin Penski as Project Engineer.

Acknowledgement is made of the assistance provided by S. K. Lee, M. Fulton, and E. Frommell of Mellon Institute.

ABSTRACT

The development of a relatively large scale inert gas reactor for use in the preparation of polystyrene via an anionic polymerization is described. The polymers were prepared with predictable molecular weights and very narrow molecular weight distributions.

Methods used to characterize and purify the samples are discussed.

This technical documentary report has been reviewed and is approved.

William E. Gibbs

William E. Gibbs
Acting Chief, Polymer Branch
Nonmetallic Materials Laboratory
Directorate of Materials and
Processes

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SUMMARY OF DATA ON POLYSTYRENE SAMPLES

Sample	M_{vc}^1	M_{vb}^2	M_p^3	f^4	\bar{M}_w/\bar{M}_n^5	Purification ⁶	S^{07}
L-II	196,000	190,000	180,000	1.09	1.015	E,F	6.06
L-V	119,000	113,000	90,000	1.32	1.055	E,F	
L-X	627,000		600,000	1.05	1.09	E	11.47
L-XIV	337,000		300,000	1.13	1.06	E	9.04
L-XV	49,000		45,000	1.09	1.05	E	2.96

¹ $\bar{M}_{vc} = \bar{M}_v$, cyclohexane. From $[\eta]_\theta = 8.45 \times 10^{-4} M^{1/2}$

² $\bar{M}_{vb} = \bar{M}_v$, benzene.⁸ From $[\eta]_{30^\circ} = 9.71 \times 10^{-5} M_v^{0.74}$

³ The predicted molecular weight from $M = \frac{\text{g monomer}}{\text{moles initiator}}$

⁴ $f = \frac{\text{molecular weight found}}{\text{molecular weight predicted}}$

⁵ Molecular weight distribution = $\frac{\text{weight average molecular weight}}{\text{number average molecular weight}}$

weight average molecular weight = $\bar{M}_w = \sum w_i n_i$

$w_i = i^{\text{th}}$ weight fraction and n_i is molecular weight of i^{th} weight fraction

$\bar{M}_n = \frac{1}{\sum w_i/n_i}$ = number average molecular weight. These ratios are based on data on the whole polymers and are maximum values.

⁶ Purification was by extraction of low molecular weight species with n-octyl alcohol (E) or by large scale fractionation (F). Two samples of L-II and L-V were sent to the Air Force, one treated by E and one by F. Thus seven samples were sent. Consult the text for an explanation of this.

⁷ The ultracentrifuge sedimentation constant in cyclohexane at 35°.

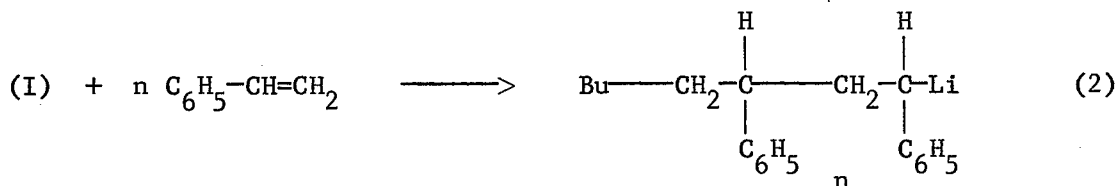
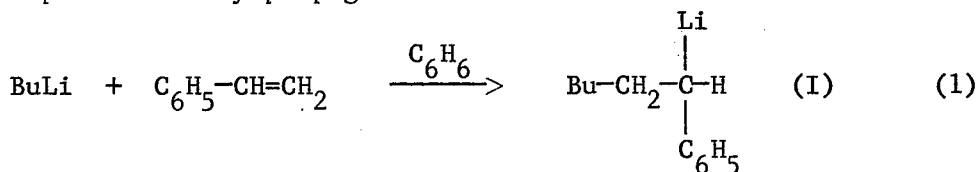
⁸ We thank Dr. V. Allen for this equation. It brings the results from measurements in cyclohexane and benzene much closer together than use of the Flory-Krigbaum equation (J. Polymer Sci. 11, 37 (1953)), $[\eta] = 1.04 \times 10^{-4} M_v^{0.73}$. Our data was measured at 25° rather than 30° but $d[\eta]/dt$ is small in benzene and no corrections have been made.

I. SYNTHETIC METHODS

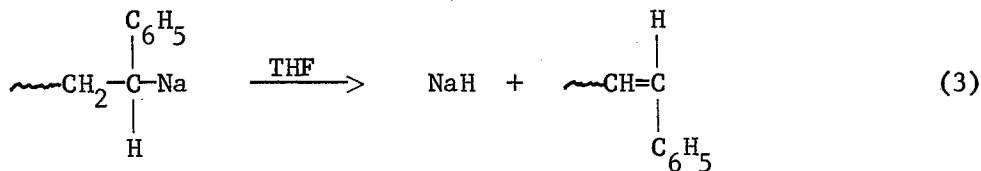
Styrene exhibits unusual reactivity in that it polymerizes well by free radical, cationic, and anionic mechanisms. The first two methods, while of great commercial importance, are not well adapted to the preparation of ultrapure research samples due to largely uncontrollable side reactions such as isomerization, disproportionation, coupling, and termination which result in products which are not completely linear and which have very broad molecular weight distributions. On the other hand, under proper conditions, anionic polymerization will yield polymers which are linear, of very narrow molecular weight distribution, and which are relatively very pure.¹

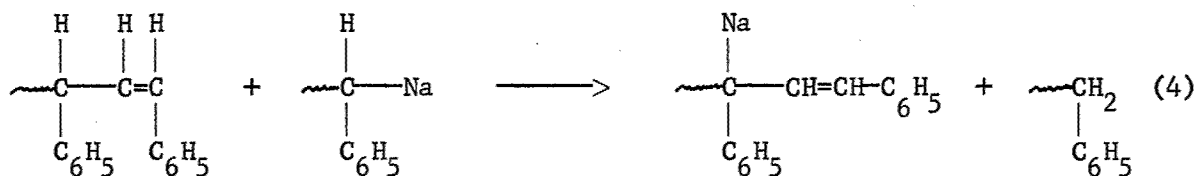
In general, two classes of anionic initiators have been most studied: (1) anion radicals such as sodium naphthalene or sodium biphenyl and (2) organometallics such as butyllithium. Since the latter was used exclusively in the work conducted here, it only need be discussed.

Initiation with butyllithium amounts to a Michael addition across the vinyl group followed by propagation:



In the propagation reaction (2) no termination steps are included. There is evidence, however, that with sodium as the cation, especially in solvents such as tetrahydrofuran, disproportionation occurs in time to give olefin and sodium hydride² followed by other terminations involving proton abstraction from the new olefinic material.

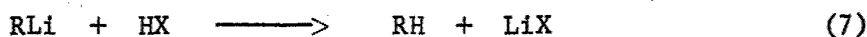
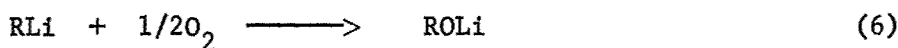
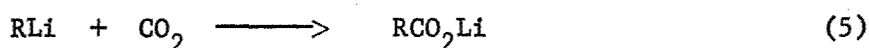




The polymerizations, however, are much faster than reactions (3) and (4) and thus the method is still of use. Interestingly the lithium system in hydrocarbon solvents exhibits a very great stability with little noticeable change over prolonged periods. In the presence of THF, however, the changes as described above do seem to occur. It might be expected that metallation of the aromatic ring might occur in the benzene-lithium system,³ but no evidence for this has been reported.

A detailed kinetic study of the butyllithium-styrene-benzene system has been reported by Worsfold and Bywater^{1d} who found that the initiation reaction was 1/6 order in butyllithium as long as its concentration did not fall below 10^{-5}M . This is due to the strong association of butyllithium in hydrocarbon solvents.⁴ It was also found that the propagation reaction was 1/2 order in styryllithium and that this reaction proceeds some 600 times faster than initiation. Although this creates problems in the control of molecular weight and distribution at low molecular weights, it does not at higher molecular weights and is of no serious consequence in the preparations undertaken in this work ($M \sim 50,000 \sim 650,000$). It should be noted that the results reported in a recent paper⁵ show that the kinetic problems discussed above can be almost entirely alleviated by conducting the polymerizations in the presence of THF. If the polymerization is conducted in 0.15 M THF (in benzene) the initiation reaction becomes virtually instantaneous (too fast to measure by normal optical methods usually used in studies of this system). Interestingly, the propagation reaction while becoming first order in styryllithium in this system (compared to 1/2 order in pure benzene) is increased only a few-fold in overall rate. All of these results are rationalized on the basis of solvation (complexing) of the active species with THF. Practically, these results are of considerable value synthetically in that it now becomes possible to prepare virtually monodisperse polystyrenes of very low molecular weight.⁶

It is necessary in work of this type that impurities be kept out of the reaction system. The impurities of concern are those which react with carbanions, e.g., oxygen, carbon dioxide, and active hydrogen compounds.

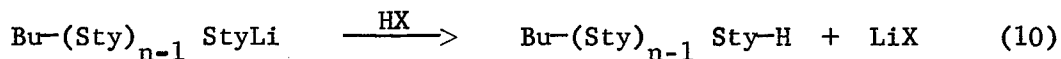
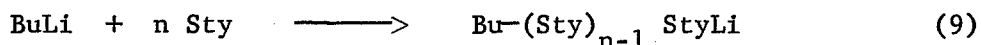


The reactions are considered to be very fast whether R in (5), (6), and (7) is butyl or styryl and in each case constitute a termination. The lithium carboxylate formed in (5) and the alkoxide formed in (6), while basic species, are assumed not to be sufficiently nucleophilic to become initiators in their own right (this assumption is applied to (7) also if X is hydroxyl) and thus are considered to be inert contaminants. Whether this is absolutely correct or whether they affect the course of the reaction somewhat by association phenomenon such as the well-known primary and secondary salt effects has not been determined. The success obtained in these polymerizations during which small amounts of some or all of these contaminants were present would indicate that they indeed have little influence over the reaction under the studied conditions.^{1a} It follows that if impurities are a factor only in the initiator, then the overall effect is to decrease the concentration of active initiator and thus increase the molecular weight. The molecular weight distribution should not be affected. On the other hand, if impurities are introduced during the course of the polymerization, it is obvious that the molecular weight distribution will be considerably broadened.⁷

Thus in very pure systems, it has been shown that polystyrene with predictable molecular weights and very narrow molecular weight distributions can be obtained by anionic polymerization. In these systems the relation between molecular weight of polymer, grams of monomer, and quantity of initiator is given by (8). In view of the preceding discussion

$$M = \frac{\text{g of monomer}}{\text{moles of initiator}} \quad (8)$$

it is seen that the end groups obtained by use of butyllithium initiation and active hydrogen termination are butyl and hydrogen, respectively.



Several factors mentioned above are worthy of further discussion in that they affect the predictability and purity of the polymers ultimately obtained. Of all the reagents used in these systems, styrene is the hardest to purify. Use of the Wenger-Yen purging technique to remove the final traces of impurities from a system previous to the actual polymerization greatly facilitates the experiments. In essence, this technique involves titration of the styrene-benzene mixture with the highly colored initiator

solution formed from butyllithium and styrene (~1:6 mole ratio) until the color persists. This is conducted in the cold and the impurities such as discussed previously presumably react much faster than the polystyrene. After this the required amount of initiator is added (equation (8)) and the polymerization is allowed to go to completion. The accuracy of predicting molecular weights using this method obviously is somewhat affected, but the convenience of the method is very attractive and molecular weights may generally be predicted to within 10-15% in our large inert gas reactor. The actual predictability ratios, i.e., \bar{M} predicted/ \bar{M} obtained are given in the Summary Table.

The way in which this procedure affects the purity of these samples is discussed fully in the next section of this report (page 7).

One phase of the present contract was to undertake the preparation of 50 g quantities of polystyrene with certain molecular weights and with each polymer to have a very narrow molecular weight distribution. The polymers were to be ultrapure and inasmuch as possible to contain only carbon and hydrogen, i.e., inert end groups. In order to achieve these ends the basic methods of Wenger and Yen,^{1a} established for vacuum line use were employed except that an inert gas reactor was developed which allowed for much larger scale runs than conveniently obtainable by high vacuum techniques. It was then possible to routinely produce 200 g batches of virtually monodisperse polymer at a time with this apparatus and it is felt that a much larger scale reaction can be achieved easily by use of the methods developed. A detailed description of the apparatus and its operation is given in the experimental section.

The success of this method can be seen from an inspection of the molecular weight distribution data listed in Tables II-VI in the Appendix. The values listed, 1.015-1.09 are maximum ones since the polymers were even further fractionated as described in the characterization section.

II. CHARACTERIZATION AND PURIFICATION OF POLYMERS

After synthesis and isolation, portions of the freeze-dried polymers were dissolved in butanone-2 (MEK; 0.2% solutions, i.e., 2 g polymer/l liter solvent), and then fractionally precipitated by incremental additions of non-solvent, methanol.⁸ Weight average (\bar{M}_w) and number average (\bar{M}_n) molecular weights were calculated by equations (11) and (12), respectively.

$$\bar{M}_w = \sum w_i M_i \quad (11)$$

$$M_n = \frac{1}{\sum w_i / M_i} \quad (12)$$

where w_i = fraction, by weight, of i^{th} fraction

M_i = molecular weight of i^{th} fraction

Integral weight distribution curves were obtained by plotting $I = \sum w_j + w_i/2$ vs. \bar{M}_i . These parameters are defined from the values obtained from a typical table of fractionation data (e.g., Tables II-VI) so that w_i is the weight fraction whose viscosity average molecular weight is \bar{M}_i . The $\sum w_j$ values are obtained by summing the weight fractions of all fractions through $i-1$. A plot of this type, while not much different from a typical weight fraction-molecular weight distribution plot in these systems of extraordinarily narrow molecular weight distribution, does recognize that the fractions obtained in a normal solution fractionation procedure do not in themselves possess infinitely narrow molecular weight distributions. It also seems to define the lower and higher molecular weight portions of a polymer more clearly upon differentiation of the integral molecular weight distribution curve.

The differential distribution curves were obtained by graphical differentiation of the $I-\bar{M}_i$ plots.⁹

Viscosity average molecular weights were obtained in benzene at 25° using equation (13) or in cyclohexane at the θ -temperature, 35°, using equation (14).

$$[\eta] = 9.71 \times 10^{-5} M^{0.74} \quad (13)$$

$$[\eta]_{\theta} = 8.45 \times 10^{-4} M^{0.5} \quad (14)$$

In the case of benzene as solvent, $[\eta]$ was determined by a one point method using equation (15), or the relationship derived in (16c).

$$[\eta] = \frac{\ln \eta_{\text{rel}}}{c} + \frac{1}{4} \left(\frac{\eta_{\text{sp}}}{c} - \frac{\ln \eta_{\text{rel}}}{c} \right) \quad (15)$$

with C in g polymer/100 ml solvent

$$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C \quad (16a)$$

$$\frac{\ln \eta_{rel}}{C} = [\eta] - k''[\eta]^2 C \quad (16b)$$

where $k'' = k' - 1/2$.¹⁰

Elimination of $[\eta]$ between equations (16a) and (16b) gives the useful relationship, (16c):

$$[\eta]^2 = \frac{2}{C} \left(\frac{\eta_{sp}}{C} - \frac{\ln \eta_{rel}}{C} \right) \quad (16c)$$

These one point determinations of intrinsic viscosity are useful approximations for experimental data where $1.6 \geq \eta_{rel} \geq 1.2$.

Intrinsic viscosities in cyclohexane were also obtained by a one point method using equation (17).

$$[\eta]_{\theta} = \frac{\ln \eta_{rel}}{C} \quad (17)$$

This arises since extrapolation of plots based on equation (18) show that k'' is nearly zero.

$$\frac{\ln \eta_{rel}}{C} = [\eta]_{\theta} - k''[\eta]_{\theta}^2 C \quad (18)$$

Infrared spectra of the various polymers (taken as films) were identical with those of standard calibration samples. The NMR spectra were all identical and not well resolved. Although at least partial resolution can be obtained by measuring the spectra of heated samples of polystyrene¹¹ no attempts to do so were made in this work.

As previously mentioned, termination with active hydrogen compounds (water, alcohol, acid) should give a hydrogen end group (equation (14)). It was felt that an easy verification of this would be accomplished by termination with tritium. Since there would be one tritium per polymer chain, this should also be a fast, expedient way to measure

number average molecular weights. Experimentally, however, it was found that an isotope effect, $k_H/k_T \approx 2.5$ was operative. This indicates that breaking of the O-H(O-T) bond occurs during the rate determining step. While interesting, any mechanistic interpretation of this would be speculative and no further work was done on this phase of the problem.

During the preceding section, the use of a convenient purging technique for final purification of the system was discussed.¹² Assuming that the major reactions occurring here are described by equations (5), (6), and (7), it is necessary at this point to discuss more fully how and why this step might introduce impurities into the system. In the case where R in these reactions is butyl, it is seen that lithium valerate, lithium amylate, and butane would be the major products. The removal of these should occur during the normal isolation procedures employed in obtaining the polymer. Thus, butane presents no problem, lithium amylate should be soluble in methyl alcohol (used as precipitant), and, to a large extent, it would be expected that lithium valerate would be also. On the other hand, the initiator, while it stoichiometrically (equation (8) should be a 1,3,5,7,9,11-hexaphenylhexadecane derivative (from a BuLi:styrene ratio of 1:6), because of the kinetic problems discussed previously is found to be a polymer of significant molecular weight. This is shown below by the fractionation data for a typical initiator prepared in benzene and then terminated with methyl alcohol.

$$\bar{M}_v(\text{bulk}) = 6600$$

(Fractionated from acetone-water)

<u>Fraction</u>	<u>Weight %</u>	<u>\bar{M}_v</u>
1	26.7	8800
2	22.9	7400
3	13.2	5600
4	13.8	3900
5	22.4	very low

In these cases R shown in (5), (6), and (7) is polymeric and the products (carboxylate and alcoholate) are polymers, with undesirable end groups which are of sufficient molecular weight to be unremovable in a simple way from the bulk polymer. Extending this reasoning, it can be argued that since no acidification steps are involved in the isolation procedure, the carbon dioxide terminated polymer should be present as a lithium salt. The alcoholate would also retain much lithium, i.e., remain as a lithium alcoholate.¹³ Finally, it is conceivable that small amounts of the other lithium-containing species are adsorbed by the precipitated polymer. These would include the C₅ systems described above as well as lithium methoxide from the normal termination. In a typical case where

200 g of polymer is prepared with a molecular weight of 100,000 and where 15% of the initiator is used for purging (i.e., 1.15 times as much as would be calculated from equation (8)) the total lithium content if it all were to remain in the polymer sample would be on the order of 80 PPM. Fortunately, emission spectroscopy was available to us so that lithium contents could be estimated.¹⁴ As can be seen in Table I, the samples contained detectable quantities of lithium.

To remove these impurities and effect a final purification of these polymers, attempts were made to run large scale fractionations on them in a specially designed 20 gallon fractionating flask. Once again MEK was used as solvent (0.5% polymer solutions) and methanol was used as non-solvent. While apparently successful, the polymers were found, after freeze-drying, to possess a persistent garlic-like odor which could be removed by prolonged treatment in the vacuum oven. One hundred grams of freeze-dried polymer was flushed for 1 hour with a vigorous stream of helium and the helium exited through dry ice-acetone and liquid nitrogen traps, respectively. Nothing detectable in the infrared (40 cc gas cell) or via gas chromatography was trapped. It was suspected that the impurity might be one of the peroxides arising from MEK. Attempts to determine whether this was the case or not by attempts to liberate iodine from iodide were inconclusive and indicated that if peroxides were present they were there in rather minute amounts. It must be concluded, therefore, that the origin and nature of this odor is not now understood. It is interesting to note that while it frequently arose in polymers obtained from MEK fractionations, it has since been detected, upon occasion, in polymers which were never in the presence of MEK.¹⁵ This serves to increase our "confusion" in this area. At any rate, samples L-II and L-V which were shipped to the Air Force several months ago were freed from this by repeated reprecipitation followed by treatment of the freeze-dried polymer at 55° in the vacuum oven. None of our tests, \bar{M}_v , distribution, i.r., NMR, were able to detect any difference between this material and the parent unfractionated polymer.

It is worthwhile to point out that these two samples were originally characterized by \bar{M}_w/\bar{M}_n values of 1.015 and 1.055, respectively. The middle fractions from the large scale fractionation were combined, redissolved, and isolated by freeze-drying. In each case approximately 10% of the highest molecular weight and 10% of the lowest molecular weight polymer was discarded. Thus the distribution values listed above are maximum values. While we have not recalculated any distribution values, these two samples are possibly the best from the standpoint of distribution ever prepared.

Since some question concerning the fractionation described above was present, it was decided to remove the majority of lithium-containing impurities by an extraction procedure. It is generally true that polymer

solubility varies inversely with molecular weight and that very low molecular weight polymers should be soluble in theta solvents at temperatures significantly below T_θ . It also seemed reasonable to expect that occlusion could be minimized by an extraction rather than precipitation method. Finally it was necessary to work in a solvent with T_θ for polystyrene sufficiently high to allow the desirable higher molecular weight materials to be insoluble at the temperature of extraction while simultaneously having this temperature above T_g so that diffusion would be rapid. Normal octyl alcohol ($T_\theta = 170^\circ$ for polystyrene)¹⁶ seemed well suited for these purposes. The amount of extraction (run at $135-140^\circ$) was dependent on temperature, time, and to an extent on the efficiency of stirring, but with the proper conditions, 2-5% of lower molecular weight species could be extracted along with some 60-70% of the original lithium. The theoretical quantity of lithium was calculated on the assumption that all of the original lithium in 200 g of polymer would be concentrated, if extraction were complete, in the extract. Details of the extraction procedure are given in the experimental section while the data is summarized in Table I.

An examination of the extracted polymers was made with the ultracentrifuge.¹⁷ Although weight average molecular weights may be obtained from measurements of this type, the actual computations were not performed. Molecular weight distributions are also obtainable by analysis of the progressive spreading of sedimentation peaks taking place during sedimentation velocity experiments.¹⁸ This was not done since it was felt that the fractionation data would suffice. Qualitatively, however, the sharp, single-peaked distribution profiles obtained indicate again the narrowness of the molecular weight distributions of these samples. Typical results are shown in Figures 14 and 15.

In Figure 14 is shown the sedimentation profiles of various monodisperse polymers. These pictures were all taken after the peak was sufficiently broken away from the meniscus and developed. Intervals of eight minutes between photographs were used. In samples of very narrow molecular weight distribution such as these, the sharp profile is maintained throughout the sedimentation. This is to be contrasted with a typical polystyrene sample prepared via thermal (free radical) polymerization. This material (Figure 15) had $\bar{M}_v = 800,000$. It not only shows a much broader sedimentation profile but also diffuses much more rapidly and photographs were taken at two minute intervals, rather than eight minute ones.

All of the ultracentrifuge measurements were made in cyclohexane at 35° , a temperature very near T_θ . The sedimentation constant, S^0 , was determined at one speed using equation (19).

$$\frac{\ln(r_p/r_o)}{w^2 t} = S^0 \left[1 - \frac{\gamma}{2} \left[\left(\frac{r_p}{r_o} \right)^2 - 1 \right] \right] \quad (19)$$

where

r_p = radial position of peak

r_o = radial position of meniscus

$$= 1/2 \gamma w^2 r_o^2 \rho^0$$

ρ^0 = solvent density at meniscus

γ = pressure coefficient in the equation

$$S(P) = S^0 [1 - \gamma P + O(P^2)]$$

Therefore, a plot of $\ln(r_p/r_o)/(w^2 t)$ versus $(r_p/r_o)^2 - 1$ extrapolated to the ordinate will give S^0 (see Figure 11). As a very good approximation, measurement of S^0 in a theta solvent may be assumed to be concentration independent¹⁹ and so measurements were made at one concentration.²⁰

It was of interest to compare our experimental results with theory. According to hydrodynamic studies, S^0 should be related to $M^{1/2}$ in a theta solvent.²¹

$$S^0 = K' M^{1/2} \quad (20)$$

or, in a general form, $S^0 = K' M^{\alpha}$. A log-log plot of S^0 versus \bar{M}_v is shown in Figure 12. Since $[\eta]_{\theta} = K M^{1/2}$, it is readily seen that $[\eta]_{\theta}$ and S^0 should be related linearly. The log-log plot of $[\eta]_{\theta}$ vs. S^0

$$S^0 = K'' [\eta]_{\theta}^{\alpha'} \quad (21)$$

where $\alpha' = 1$

is shown in Figure 13.

III. EXPERIMENTAL

A. Preparation of Polymers in the Inert Gas Reactor

A general description of the inert gas reactor and procedure will be given. In certain instances high vacuum techniques were used, especially at the onset of this work, but excellent detailed procedures of this method may be found in the literature.^{1b}

The apparatus consists presently of a 3-l 5-necked flask (24/40 ground glass; female joints) with a large capillary exit tube extending from the bottom around the side and to which is affixed a 3-way stopcock. Solutions are forced out of the flask via this tube by a positive gas pressure. The reactor is equipped by means of the necks and appropriate Y-tubes with a vacuum joint or mercury seal stirrer; dropping funnels for monomer, initiator, and terminator; inlet for the direct introduction by distillation of solvent; condensers culminating in gas outlet tubes attached to mercury bubble traps; gas inlets and thermometers. All dropping funnels are pressure self-regulating and calibrated volumetrically. The one used for initiator (250 ml capacity) is further modified to include a mercury seal stirrer; gas inlet and outlet; syringe cap opening for introduction of reagents and removal of samples for analysis; and a condenser through which pure solvent can be introduced directly by distillation. All gas outlets contain stopcocks which can be closed in operations, during which solutions are forced out of the reactor by positive pressure.

The initiator is prepared by first distilling into the dropping funnel described above the required amount of purified benzene. The benzene purification is accomplished by distilling it from a solution of butyl- and styryllithium anions formed by the reaction of butyllithium²² with styrene in the mole ratio of ca. 1:6. Next a solution of butyllithium in hexane is introduced via the syringe (concentration between 0.1-0.5 normal). This is followed by a similar introduction of distilled styrene. The solution is then heated with a heat gun blower at $\sim 60^\circ$ for 12 hours to convert all of the styrene to styryllithium. The preceding steps all take place under nitrogen or argon, or both, purified by passing through a benzene solution of butyl-styryllithium. After this heating period, a sample of the initiator is removed and analyzed²³ by the double titration procedure. Typically these solutions thus prepared have been about 5×10^{-2} N in active anion.

The reactor proper after normal cleaning and drying is charged with a solution of butyl-styryllithium in reagent benzene (about 0.1 N) and this is thoroughly stirred under reflux under nitrogen or argon for a period of 1 hour. The narrow molecular weight distributions of the polymers prepared in the reactor are sufficient indication that this procedure

cleans the system very thoroughly. Upon cooling, the gas exit stopcocks are closed and the anion solution is forced out of the reactor via the capillary. Pure benzene is distilled in to rinse the system and this too is then removed. The required amount of pure benzene is then distilled in with cooling. Typically 200 g batches of polymer are prepared so that 2,000 ml of benzene are used in order to form a 10% solution. The benzene is cooled to $\sim 5^\circ$ and then titrated with as much initiator as needed to form a persistent light yellow color. This normally involves between 1 and 3 ml ($5-15 \times 10^{-5}$ mole). The styrene is freshly distilled directly into a dropping funnel under nitrogen. It is then degassed and stored, if necessary, at dry ice temperatures. The required amount is added to the cold benzene and this is then titrated at 5° or slightly less until a yellow color persists.²⁴ With well distilled and degassed styrene, 5-8 ml of 5×10^{-2} N solution has been necessary for 200 g batches, i.e., $25-40 \times 10^{-5}$ mole. Typically, with batches of this size (200 g) on the order of 10-20% of the total initiator solution added (depending on the desired molecular weight) is used to purge impurities.

Having titrating the impurities, the calculated amount (equation (10)) of initiator is added (15-100+ ml of 5×10^{-2} N solution depending on the polymer molecular weight) and the ice bath is replaced by a hot water bath at 50° . The red-orange color gradually becomes more intense as all of the butyllithium not previously converted to styryllithium reacts (this occurs over a period of 45-60 minutes). It is also noted that after about 20 minutes the reaction temperature reaches a maximum of about 60° and then gradually falls back to the bath temperature after about an hour. A total of two hours reaction time is allowed, after which termination is brought about by addition of pure methanol or, in some cases as discussed above, tritium labeled water. The polymer solution is then forced out of the reactor and precipitated by slow addition to a large excess of cold methanol. The precipitated polymer is collected and washed with distilled and deionized water to remove lithium salts and then dried by sucking on a filter and ultimately in a vacuum oven. Yields are essentially quantitative.

B. Polymer Fractionation

The polymers prepared as described above were fractionated from MEK (0.2% solution) by incremental addition of methanol. The fractionations were carried out in pear-shaped flasks of appropriate sizes and all work was performed in thermostated baths held at $30 \pm 0.05^\circ$. The various fractions which precipitated were removed via pipettes, dissolved in benzene, filtered, freeze-dried, weighed, and submitted to molecular weight determinations via the viscometric procedures discussed previously.

Large scale fractionations were performed in a similar fashion except that the vessel had a 20 gallon capacity and the polymer

concentration was increased to 0.5%.

C. Normal Octanol Extraction of Polystyrene

A round-bottom flask equipped with an efficient mechanical stirrer, nitrogen inlet (of sufficient length to reach beneath the surface of the liquid), thermometer, and condenser was filled with 55-70 g of polymer and sufficient reagent grade n-octyl alcohol so that there was ~5 g polymer/100 cc alcohol. This mixture was heated and stirred at 135-140°C for ~5 hours while vigorously bubbling nitrogen through the solution. At the end of this period the stirrer was stopped and the polymer allowed to settle (nitrogen flow maintained until the polymer reached room temperature). The supernatant liquid was siphoned off. The polymer remaining was dissolved in benzene, precipitated in methanol, redissolved in benzene and freeze-dried in the usual way. The octyl alcohol which had been removed was distilled in vacuo until the remaining volume was ~200 ml. This residue was then allowed to cool to room temperature. Methanol (ca. 5 volumes) was added and the precipitate was filtered, dried, weighed, and analyzed. For low molecular weights (under 100,000) the procedure was the same except that lower temperatures (125-130°) were used. The results obtained are shown in Table I.

IV. REFERENCES

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(d) D. J. Worsfold and S. Bywater, Can. J. Chem. 38, 1891 (1960).
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2. G. S. Spach, M. Levy, and M. Szwarc, J. Chem. Soc. 1962, 355;
M. Levy, M. Szwarc, S. Bywater, and D. J. Worsfold, Polymer 4, 515 (1960).
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6. This has been checked in these laboratories by T. Altares and D. P. Wyman in conjunction with another problem and the results are gratifying.
7. A mathematical analysis of these factors is given by T. A. Orofino and F. Wenger, J. Chem. Phys. 35, 532 (1961). See also F. Wenger, ONR Technical Report No. 5 (Nonr 2693(00), Task No. NR 356-407), September 1960-February 1961.
8. Details of this procedure are given in the experimental section and tables of fractionation data in the appendix.
9. At any point in the integral curve dI/dM_i is equal to the tangent of the curve at this point. These new points (i.e., the tangents) plotted against M_i give the differential distribution curve.
10. P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953; p. 310.
11. S. Brownstein, S. Bywater, and D. J. Worsfold, Symposium on Spectroscopy of High Polymers, 142nd National Meeting, American Chemical Society, Atlantic City, New Jersey, September 1962.

12. See the experimental section for more details concerning this.
13. See E. F. Caldin and G. Long, *Nature* 172, 583 (1953) concerning this matter.
14. We thank Dr. E. S. Hodge and B. L. Ely for these determinations.
15. We thank Dr. V. R. Allen for bringing this to our attention.
16. We thank Dr. T. Orofino for this information.
17. We are indebted to Mr. R. E. Kerwin for these measurements and the calculation of the sedimentation constants.
18. R. Signer and H. Gross, *Helv. Chim. Acta.* 17, 726 (1934).
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20. As a convenient guide we used $\text{wt } \% = 180/\sqrt{M}$.
21. Strictly speaking, this should apply to \bar{M}_w , but with polymers of very narrow molecular weight distribution \bar{M}_w , \bar{M}_v , and \bar{M}_n are almost synonymous so \bar{M}_v was used here.
22. In this step and all others in which butyl-styryllithium species are used for purification it has been found most convenient to use butyl-lithium in wax, available from the Lithium Corporation of America, as precursor.
23. H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.* 66, 1515 (1944).
24. This method, developed by Wenger and Yen (reference 1a), is very convenient and time-saving. Of all the reagents used, styrene is the hardest to purify and without this purging step, distillation from alkali metal ketyls and the like is necessary.

V. APPENDIX
OF TABLES AND ILLUSTRATIONS

TABLE I

EXTRACTION OF POLYSTYRENE WITH OCTYL ALCOHOL

Polymer Sample	\bar{M}_v	Extract \bar{M}_v	% extracted	PPM Li in sample	PPM Li in extract	Theory	% Li extracted
L-2	196,000	145,000	2.61	15	390	580	68
L-5	118,000	42,000	5.11	25	350	490	71
L-10	629,000	180,000	4.68	--	200		
L-14	352,000	187,000	5.01	--	200		
L-15	44,000	15,000	4.29	20	280	460	61

TABLE II

L-II - POLYSTYRENE

4.0091 g/2000 ml
MEK - 30°C

$[\eta] = 0.7822$

$\bar{M}_v = 190,000$

FRACTIONATION DATA

Viscosity solvent
Benzene, 25.0°C

Fraction	$\frac{\text{cc MeOH}}{100 \text{ cc MEK}}$	$\frac{\text{g}}{\text{fraction}}$	Wt. %	Total %	$[\eta]$	\bar{M}_v	$\frac{\bar{M}_w}{\bar{M}_n} = 1.015$
1 (400 ml CP + 6)	20.30	0.3120	7.78	7.78	0.860	216,000	
2	20.45	0.4234	10.56	18.34	0.817	201,000	
3	20.70	0.3463	8.64	26.98	0.811	199,000	
4	20.92	0.4867	12.14	39.12	0.794	194,000	
5	21.17	0.5866	14.63	53.75	0.786	191,000	
6	21.52	0.1800	4.49	58.24	0.788	192,000	
7	22.02	0.4058	10.12	68.36	0.781	190,000	
8	22.37	0.2463	6.14	74.50	0.775	187,000	
9	22.77	0.2302	5.74	80.24	0.776	187,000	
10	23.17	0.1754	4.38	84.62	0.766	185,000	
11	23.58	0.1935	4.83	89.53	0.766	185,000	
12	24.18	0.1088	2.71	92.16	0.765	184,000	
13	25.30	0.1303	3.25	95.41	0.749	179,000	
14	evapd.	0.1815	4.53	99.94	0.534	113,000	

TABLE III

L-V - POLYSTYRENE

4.0027 g/2000 ml MEK

FRACTIONATION DATA

Viscosity solvent
Cyclohexane, 34.5°C

$$[\eta]_{\theta} = 0.2902$$

$$\bar{M}_{v,\theta} = 117,900$$

Fraction	$\frac{\text{cc MeOH}}{100 \text{ cc MEK}}$	$\frac{\text{g}}{\text{fraction}}$	$\frac{\text{Wt. \%}}{\text{fraction}}$	Total %	$[\eta]_{\theta}$	\bar{M}_v	
1 (415 ml CP)	21.15	0.0457	1.142	1.142	0.537	405,000	
	**						
2	23.05	0.0769	1.921	3.063	0.365	186,000	$[\eta]_{\text{benzene}} = 0.5330$
3	23.40	0.1335	3.335	6.398	0.322	145,000	
4	24.00	0.8010	20.011	26.409	0.303	128,000	$\frac{\bar{M}_v}{\bar{M}_n} = 1.055$
5	24.80	0.9800	24.483	50.892	0.298	124,000	
6	25.80	0.7448	18.607	69.499	0.294	121,000	
7	26.35	0.2069	5.169	74.668	0.292	119,000	
8	27.00	0.2508	6.266	80.934	0.291	119,000	
9	27.85	0.2173	5.429	86.363	0.292	119,000	
10	29.00	0.1740	4.347	90.710	0.282	111,000	
11	30.65	0.1424	3.558	94.268	0.265	98,000	
12	evapd.	0.2281	5.699	99.97	0.207	60,000	

$$\bar{M}_w = 1.2346 \times 10^5$$

Equations:
$$[\eta]_{\theta} = \frac{\ln[\eta_{\text{rel}}]}{c}$$

$$\bar{M}_n = 1.1701 \times 10^5$$

$$M_{\theta} = \left(\frac{[\eta]}{k \times g^{1/2}} \right)^2$$

$$k = 8.45 \times 10^{-4}$$

$$g = 1$$

** Seven day interval between fractions.

TABLE IV

L-X - POLYSTYRENE

4.0100 g/2000 ml MEK

FRACTIONATION DATA

Viscosity solvent
Cyclohexane, 34.5°C

$$[\eta]_{\theta} = 0.6722$$

$$\bar{M}_v = 627,100$$

Fraction	cc MeOH 100 cc MEK	g fraction	Wt. %	Total %	$[\eta]_{\theta}$	M_v	
1 (320 ml CP)	16.15	0.3158	7.875	7.875	0.74	757,000	$\frac{\bar{M}_w}{\bar{M}_n} = 1.09$
2	16.40	0.4212	10.504	18.379	0.71	699,000	
3	16.65	0.6753	16.840	35.219	0.70	683,000	
4	16.85	0.5161	12.870	48.089	0.69	674, 00	$\bar{M}_w = 6.29 \times 10^4$
5	17.08	0.4006	9.990	58.079	0.69	660,000	$\bar{M}_n = 5.73$
6	17.30	0.2509	6.257	64.336	0.68	655,000	
7	17.55	0.2969	7.404	71.740	0.67	633,000	
8	18.05	0.3296	8.219	79.959	0.67	620,000	
9	18.45	0.2246	5.601	85.560	0.66	617,000	
10	19.15	0.1757	4.382	89.942	0.63	563,000	
11	20.40	0.1466	3.656	93.598	0.58	470,000	
12	evapd.	0.2557	6.377	99.975	0.38	205,000	

Equations:
$$[\eta]_{\theta} = \frac{\ln[\eta_{rel}]}{c}$$

$$\bar{M}_v = \left(\frac{\eta}{k g^{1/2}} \right)^2$$

$$k = 8.45 \times 10^{-4}$$

$$g = 1$$

TABLE V

L-XIV - POLYSTYRENE FRACTIONATION DATA

4.0000g/2000 MI MEK

 $[\eta]_{\theta} = 0.4906$ $\bar{M}_{V,\theta} = 337,100$ Viscosity Solvent
cyclohexane, 34.5°C.

Fraction	cc M.OH 100 cc MEK	gram Fraction	wt. % Fraction	Total %	$[\eta]_{\theta}$	\bar{M}_V
1	17.90	0.2664	6.660	6.660	0.5841	478,000
2	18.10	0.0828	2.070	8.730	0.5379	405,000
3	18.35	0.2769	6.923	15.653	0.5299	393,000
4	18.55	0.0512	1.280	16.933	0.5196	378,000
5	18.95	0.3357	8.393	25.326	0.5203	379,000
6	19.40	0.8683	21.708	47.034	0.5172	375,000
7	19.75	0.3638	9.095	56.129	0.5117	367,000
8	20.05	0.2144	5.360	61.489	0.5100	364,000
9	20.35	0.3013	7.533	69.022	0.5078	361,000
10	20.90	0.2354	5.885	74.907	0.5057	358,000
11	21.55	0.3118	7.795	82.702	0.4941	342,000
12	22.40	0.2456	6.140	88.842	0.4746	316,000
13	23.55	0.1582	3.955	92.797	0.4345	264,000
14	25.40	0.1372	3.430	96.227	0.3826	205,000
15	evaporated	0.1400	3.500	99.727	0.2424	117,000

 $[\eta]_{\text{cyclohexane}} = 0.4906$ $\bar{M}_V_{\text{cyclohexane}} = 337,100$ $\bar{M}_w/\bar{M}_n = 1.06$

$$\text{Equations: } [\eta]_{\theta} = \frac{\ln[\eta_{\text{vel}}]}{C}$$

$$\bar{M}_{\theta} = \left(\frac{[\eta]}{K} \right)^2$$

$$K = 8045 \times 10^{-4}$$

$$\bar{M}_w = 3.5400 \times 10^5$$

$$\bar{M}_n = 3.3400 \times 10^5$$

TABLE VI

L-XV - POLYSTYRENE FRACTIONATION DATA

3.7500g/1875 MI MEK

 $[\eta]_{\theta} = 0.1877$ $\bar{M}_{V,\theta} = 49,300$ Viscosity Solvent
cyclohexane, 34.5°C.

Fraction	cc M OH 100cc MEK	gram Fraction	wt.% Fraction	Total %	$[\eta]_{\theta}$	\bar{M}_V
1	29.39	0.3607	9.619	9.619	0.2119	63,000
2	29.81	0.1861	4.963	14.582	0.2089	61,000
3	30.35	0.2523	6.728	21.310	0.2075	60,000
4	30.88	0.3120	8.320	29.630	0.2041	58,000
5	31.57	0.3720	9.920	39.550	0.2027	58,000
6	32.48	0.3859	10.291	49.841	0.2004	56,000
7	33.60	0.3294	8.784	58.625	0.1971	54,000
8	34.93	0.3259	8.691	67.316	0.1877	49,000
9	36.53	0.2613	6.968	74.284	0.1870	49,000
10	38.45	0.2153	5.741	80.025	0.1790	45,000
11	40.59	0.1511	4.029	84.054	0.1679	40,000
12	43.25	0.1130	3.013	87.067	0.1582	35,000
13	46.83	0.1096	2.923	89.990		
14	50.77	0.0613	1.635	91.625	0.1041	15,000
15	evaporated	0.1746	4.656	96.281		

22

 $[\eta]_{\text{cyclohexane}} = 0.1877$
 $\bar{M}_V_{\text{cyclohexane}} = 49,300$
 $\bar{M}_w/\bar{M}_n = 1.051$

$$\bar{M}_w = 4.9157 \times 10^4 \quad \text{Equations: } [\eta] = \frac{\ln[\eta_{\text{rel}}]}{C}$$

$$\bar{M}_n = 4.6785 \times 10^4 \quad \bar{M}_{\theta} = \left(\frac{[\eta]}{K} \right)^2$$

$$K = 8.45 \times 10^{-4}$$

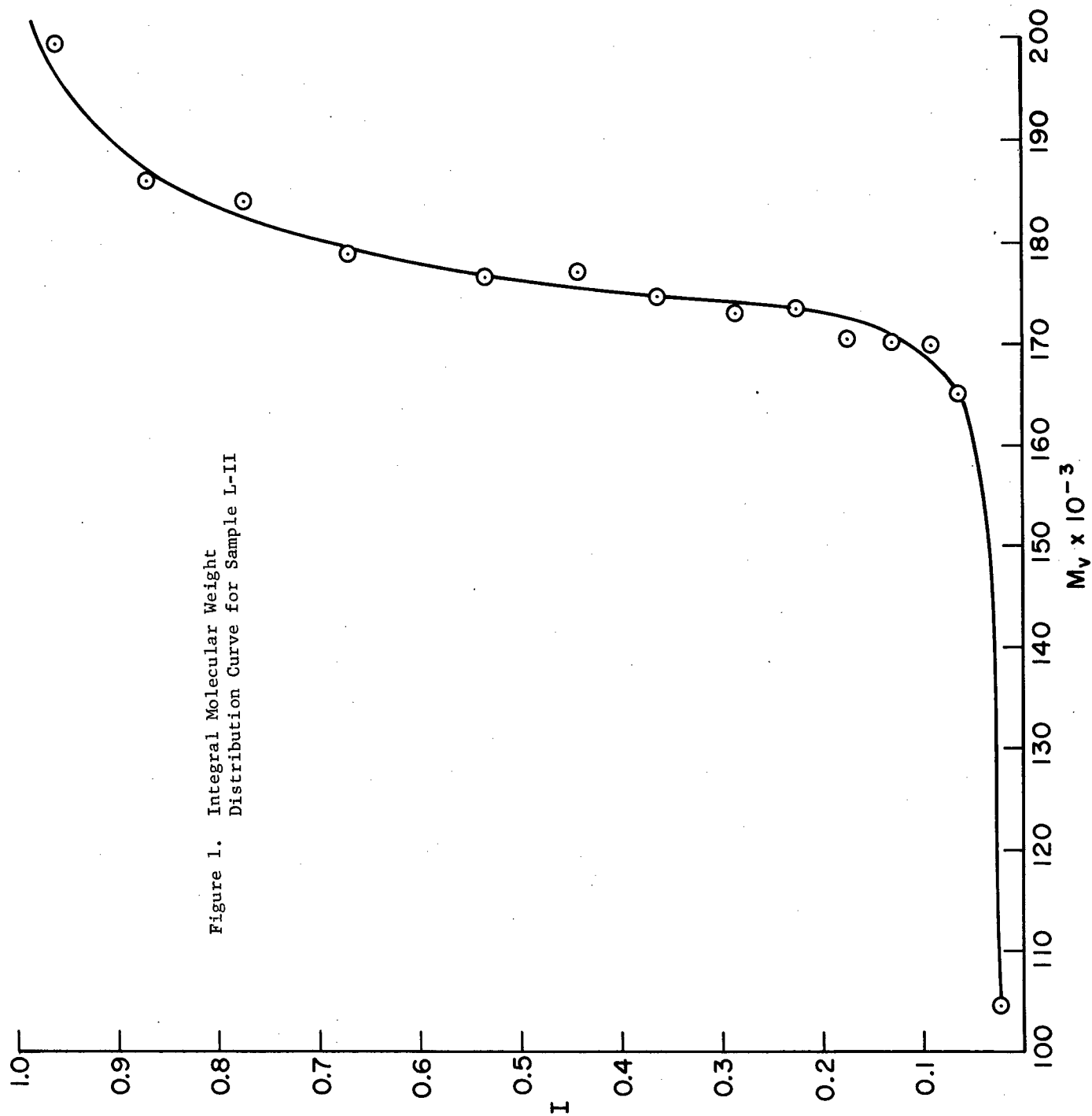
TABLE VII
ULTRACENTRIFUGE DATA

Species	t(sec)	r_o	r_p	r_p/r_o	$(r_p/r_o)^2$	$\log (r_p/r_o)$	$\frac{2.3}{w^2 t \times 10^{-13}}$	$\frac{\ln (r_p/r_o)}{w^2 t \times 10^{-13}}$	$(r_p/r_o)^2 - 1$
PS - L2	1620	6.020	6.200	1.0299	1.0607	.012795	467.68	5.984	.0607
52,640 RPM	2100	6.020	6.254	1.0389	1.0793	.016574	360.79	5.980	.0793
8 min. int.	2580	6.020	6.307	1.0477	1.0976	.020237	293.65	5.943	.0976
$w^2 = 30.387 \times 10^6$	3060	6.020	6.360	1.0565	1.1161	.023870	247.61	5.910	.1161
	3540	6.020	6.413	1.0653	1.1349	.027472	214.02	5.880	.1349
	4020	6.020	6.466	1.0741	1.1537	.031045	188.48	5.851	.1537
	4500	6.020	6.518	1.0827	1.1722	.034508	168.37	5.810	.1722
PS - L14	1620	5.941	6.203	1.0441	1.0901	.018742	467.68	8.765	.0901
52,640 RPM	2100	5.941	6.279	1.0569	1.1170	.024034	360.79	8.671	.1170
	2580	5.941	6.355	1.0697	1.1443	.029262	293.65	8.593	.1443
	3060	5.941	6.429	1.0821	1.1709	.034267	247.61	8.485	.1709
	3540	5.941	6.503	1.0946	1.1981	.039255	214.02	8.401	.1981
	4020	5.941	6.578	1.1072	1.2259	.044226	188.48	8.336	.2259
	4500	5.941	6.653	1.1198	1.2540	.049141	168.37	8.274	.2540

TABLE VIII
ULTRACENTRIFUGE DATA

Species	t(sec)	r _o	r _p	r _p /r _o	(r _p /r _o) ²	log (r _p /r _o)	$\frac{2.3}{w^2 t \times 10^{-13}}$	$\frac{\ln (r_p/r_o)}{w^2 t \times 10^{-13}}$	(r _p /r _o) ² - 1
PS - L 10	1020	6.009	6.280	1.0451	1.0922	.019158	572.27	10.964	.0922
59,780 RPM	1500	6.009	6.399	1.0649	1.1340	.027309	389.15	10.627	.134
8 min. int.	1980	6.009	6.516	1.0844	1.1759	.035190	294.81	10.374	.1759
w ² = 39.4468x10 ⁶	2460	6.009	6.631	1.1035	1.2177	.042772	237.28	10.149	.2177
	2940	6.009	6.743	1.1222	1.2593	.050070	198.54	9.9409	.2593
	3420	6.009	6.855	1.1408	1.3014	.057210	170.68	9.765	.3014
	3900	6.009	6.963	1.1588	1.3428	.064009	149.67	9.580	.3428
	4380	6.009	7.071	1.1768	1.3849	.070703	133.27	9.4226	.3849
PS - L-15	1020	6.009	6.081	1.0120	1.0241	.005181	572.27	2.965	.0241
59,780 RPM	1500	6.009	6.116	1.0178	1.0359	.007662	389.15	2.982	.0359
8 min. int.	1980	6.009	6.152	1.0238	1.0482	.010215	294.81	3.0115	.0482
	2460	6.009	6.189	1.0300	1.0609	.012837	237.28	3.046	.0609
	2940	6.009	6.224	1.0358	1.0729	.015276	198.54	3.033	.0729
	3420	6.009	6.261	1.0420	1.0858	.017868	170.68	3.050	.0858
	3900	6.009	6.296	1.0478	1.0979	.020278	149.67	3.035	.0979
	4380	6.009	6.333	1.0539	1.1107	.022799	133.27	3.038	.1107

Figure 1. Integral Molecular Weight
Distribution Curve for Sample L-II



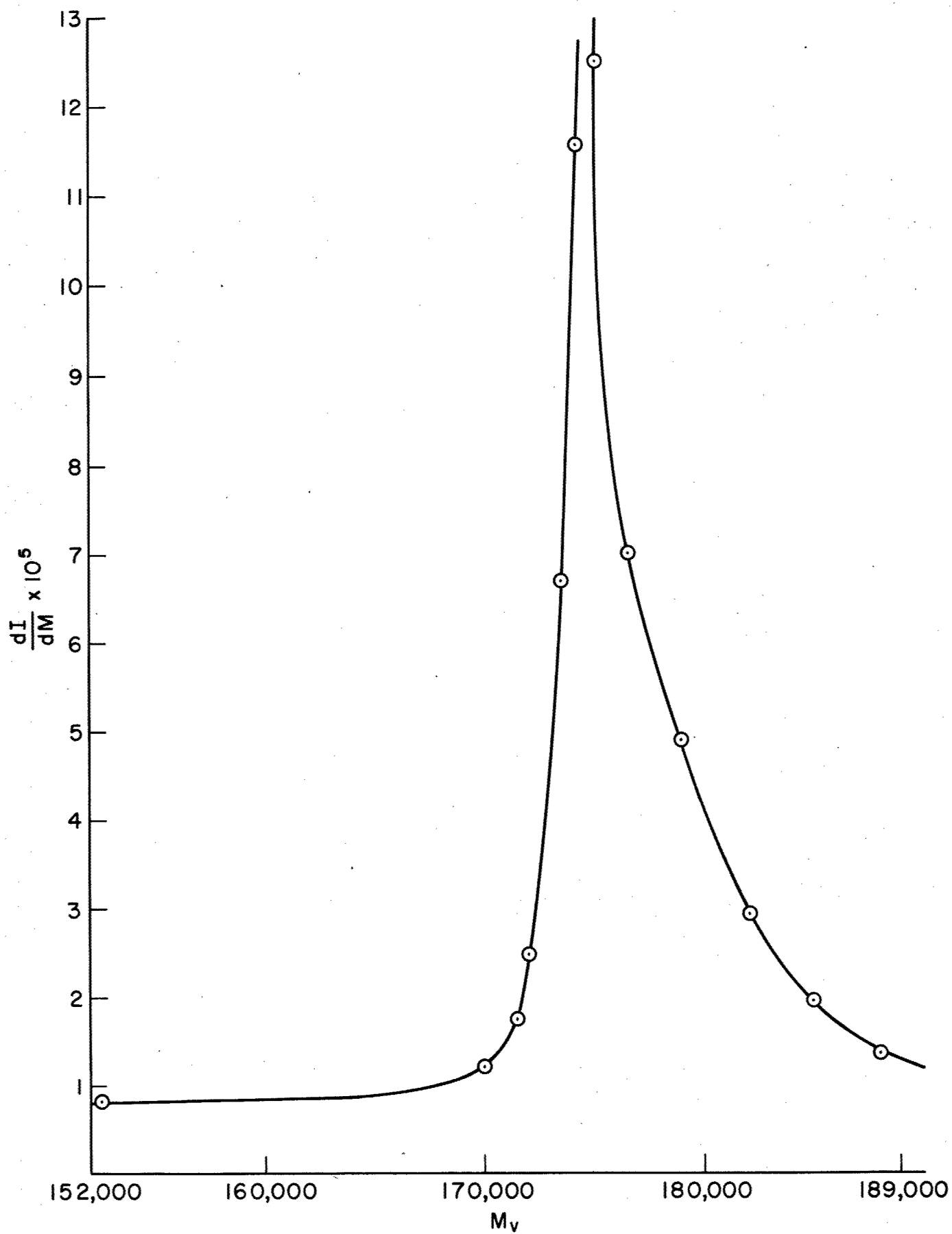
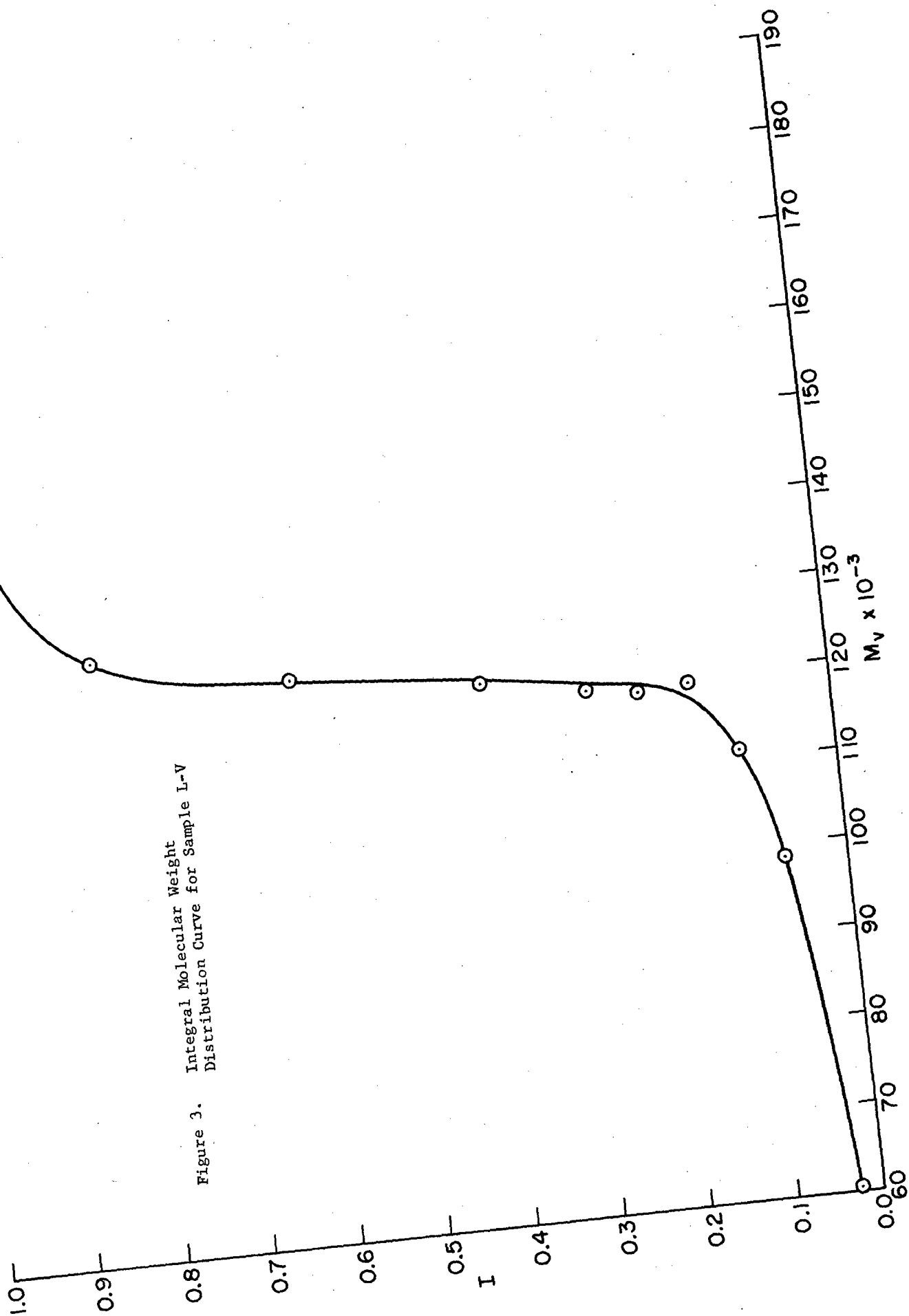


Figure 2. Differential Molecular Weight Distribution Curve for Sample L-II



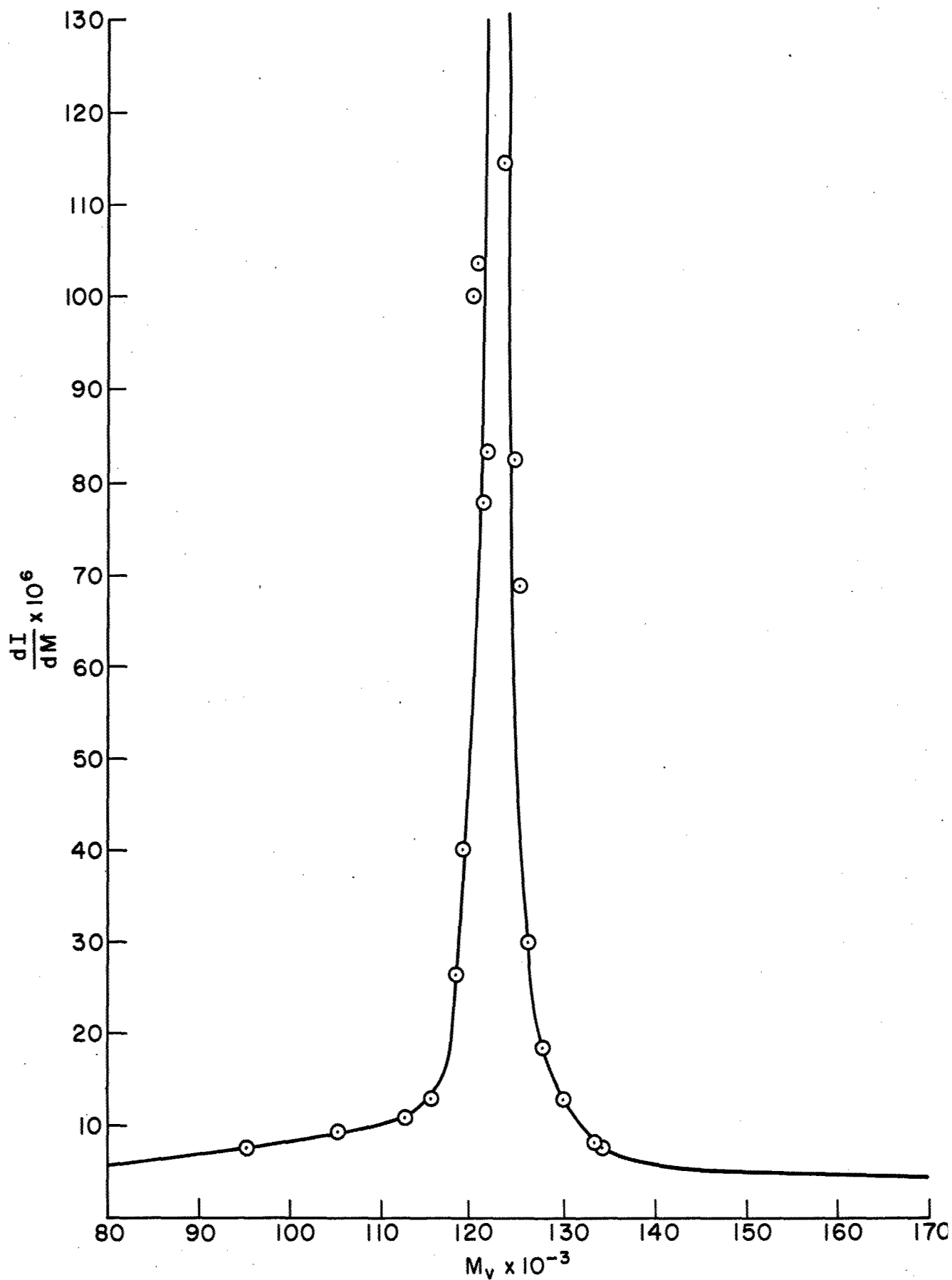
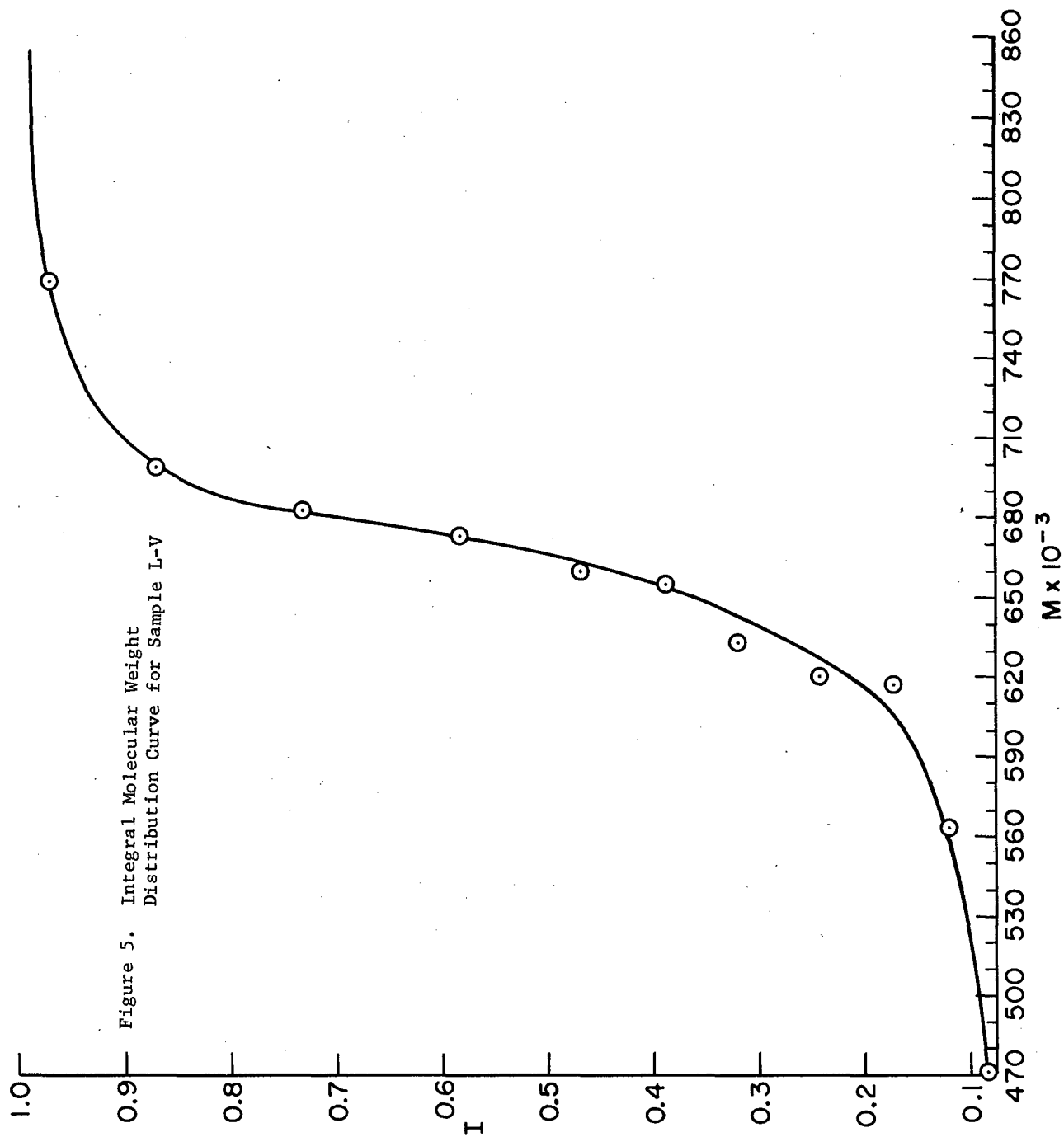


Figure 4. Differential Molecular Weight Distribution Curve for Sample L-V



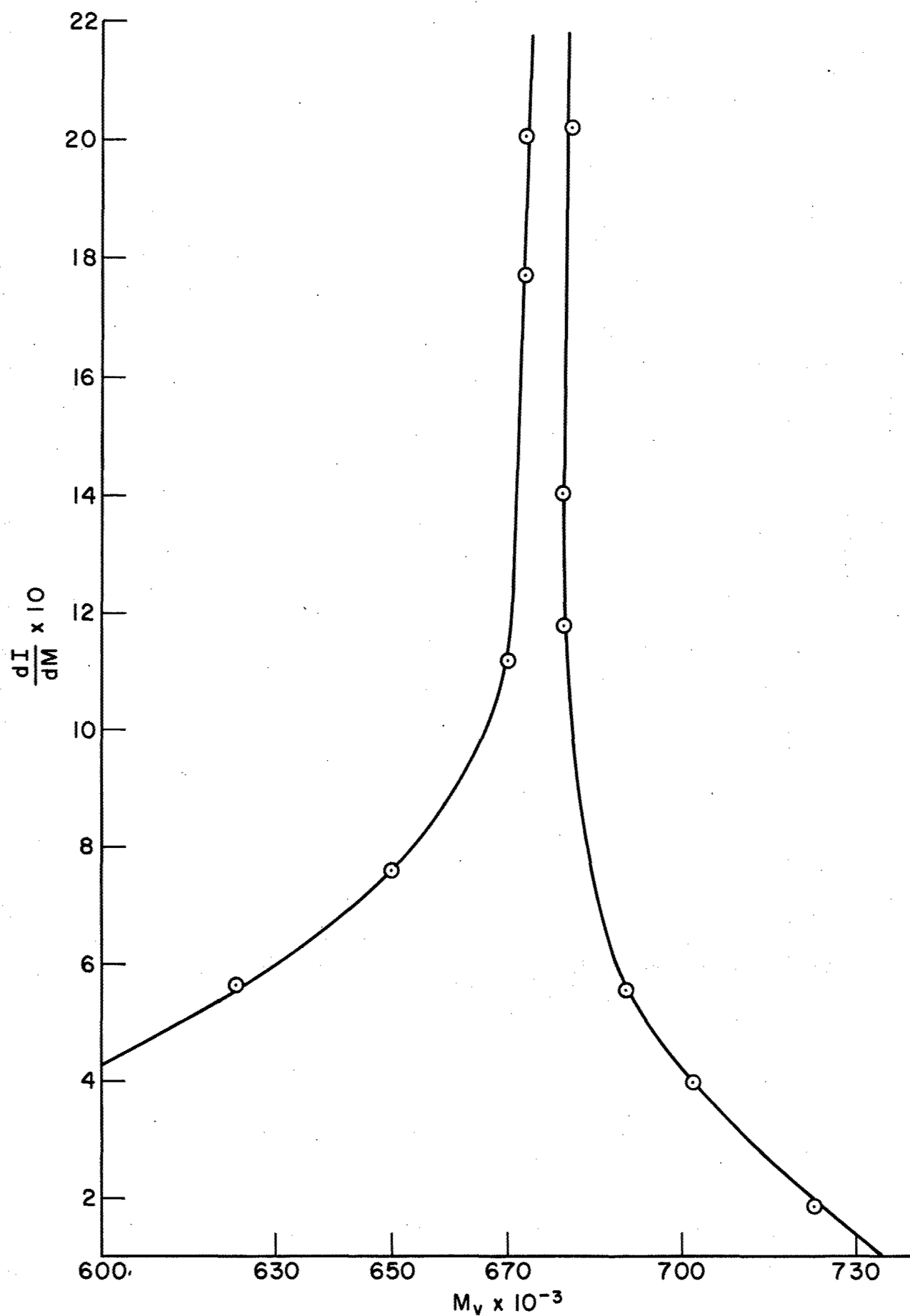


Figure 6. Differential Molecular Weight Distribution Curve for Sample L-X

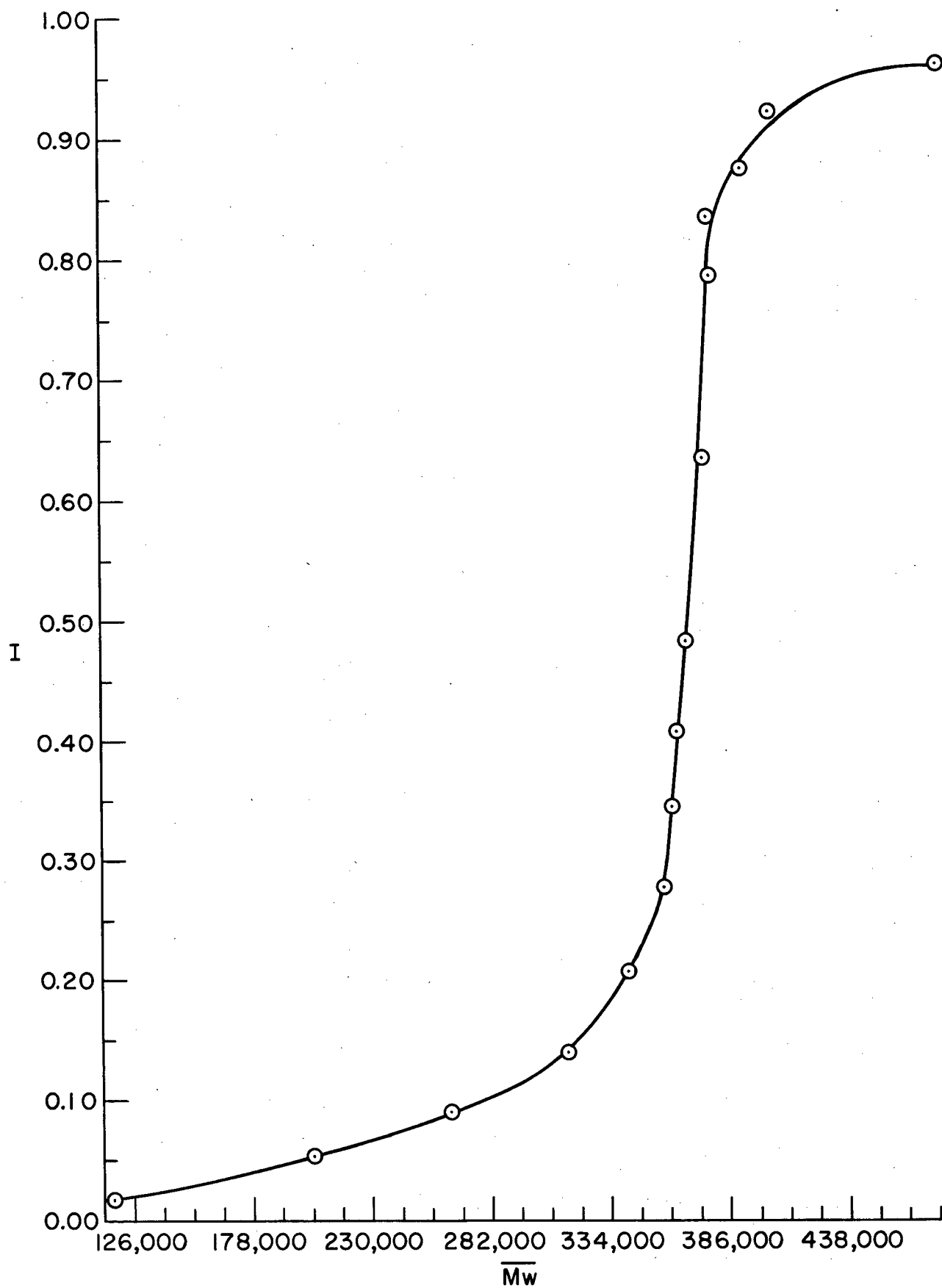


Figure 7. Integral Molecular Weight Distribution Curve for Sample L-XIV

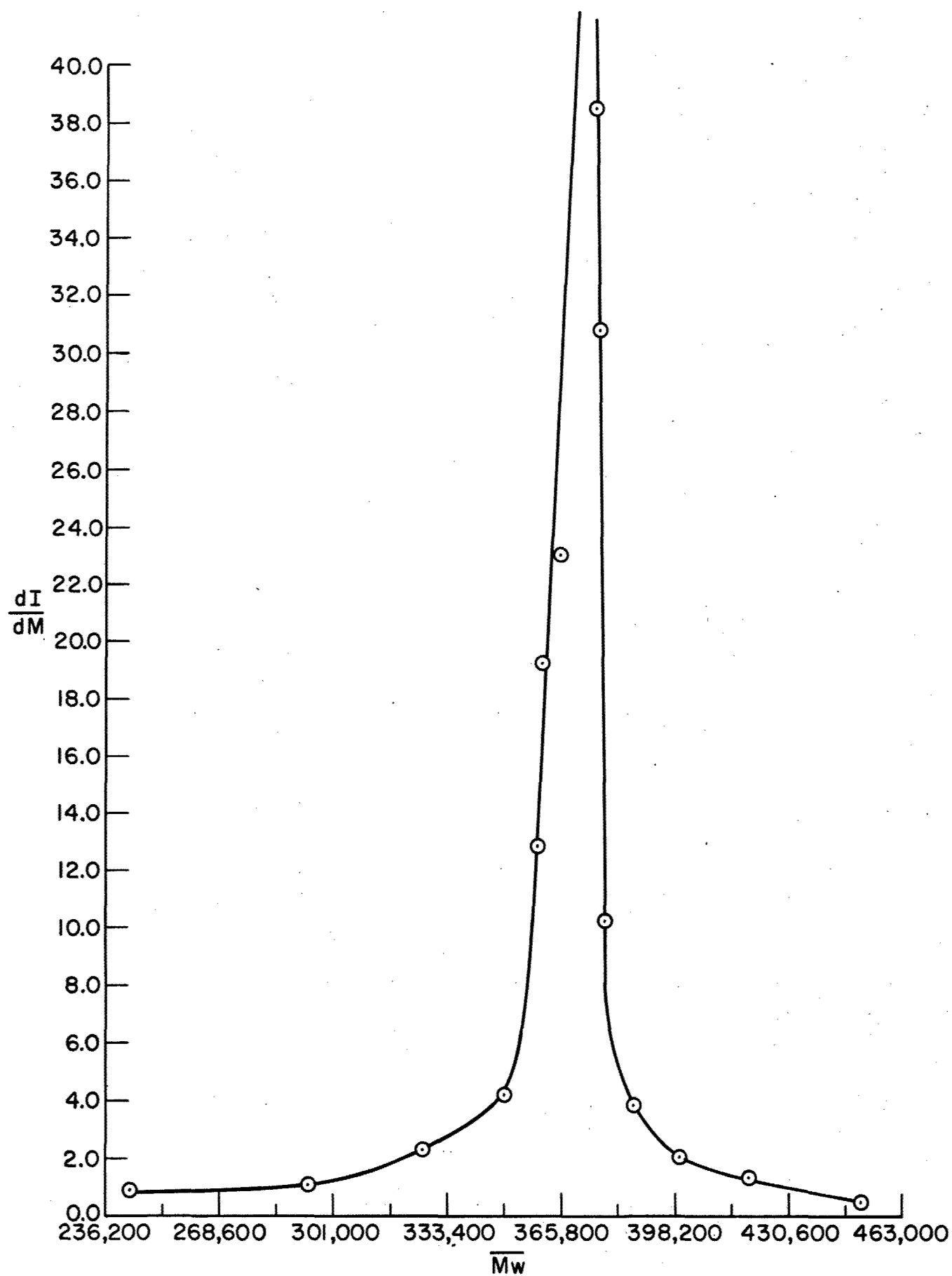


Figure 8. Differential Molecular Weight Distribution Curve for Sample L-XIV

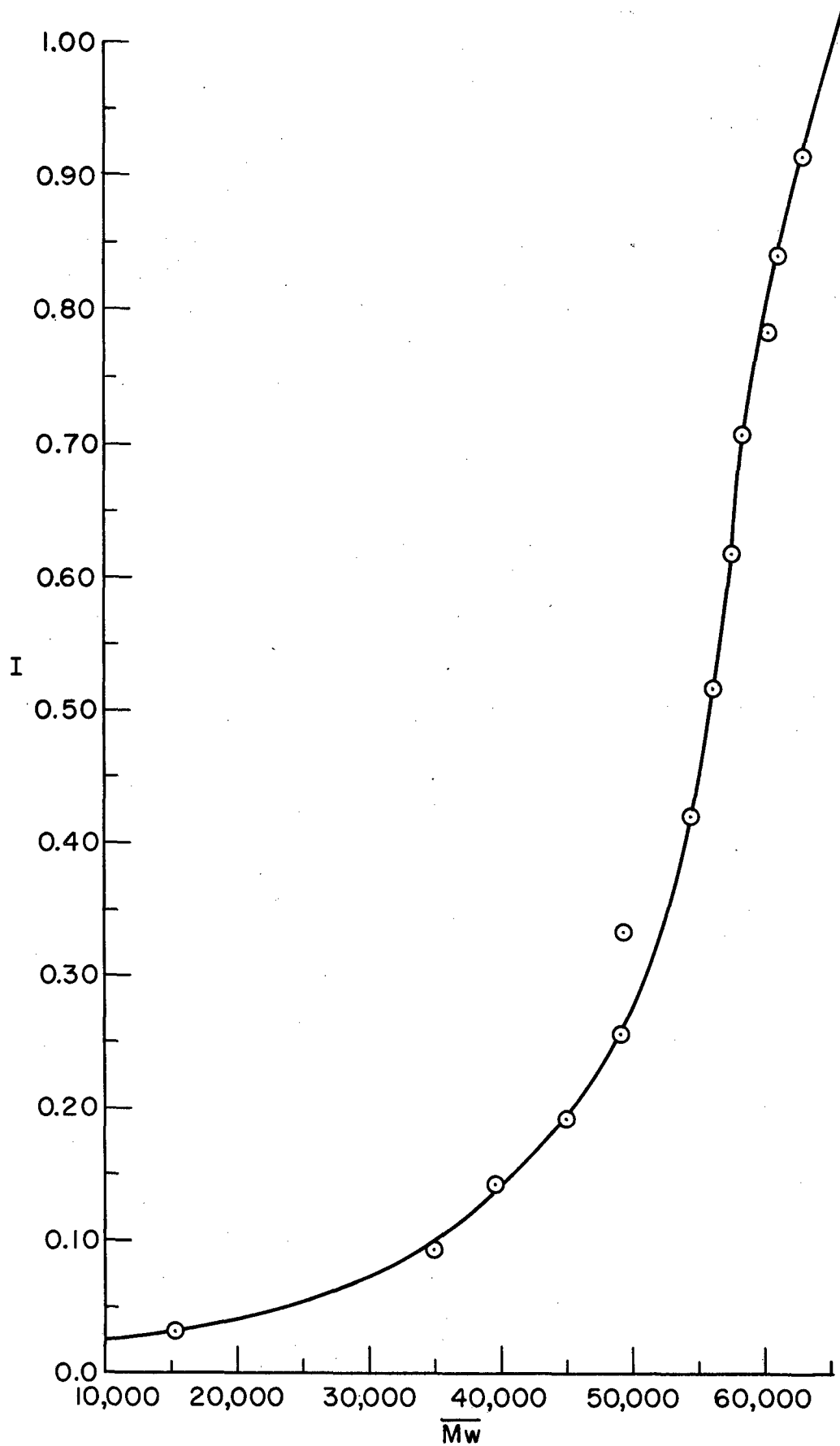


Figure 9. Integral Molecular Weight Distribution Curve for Sample L-XV

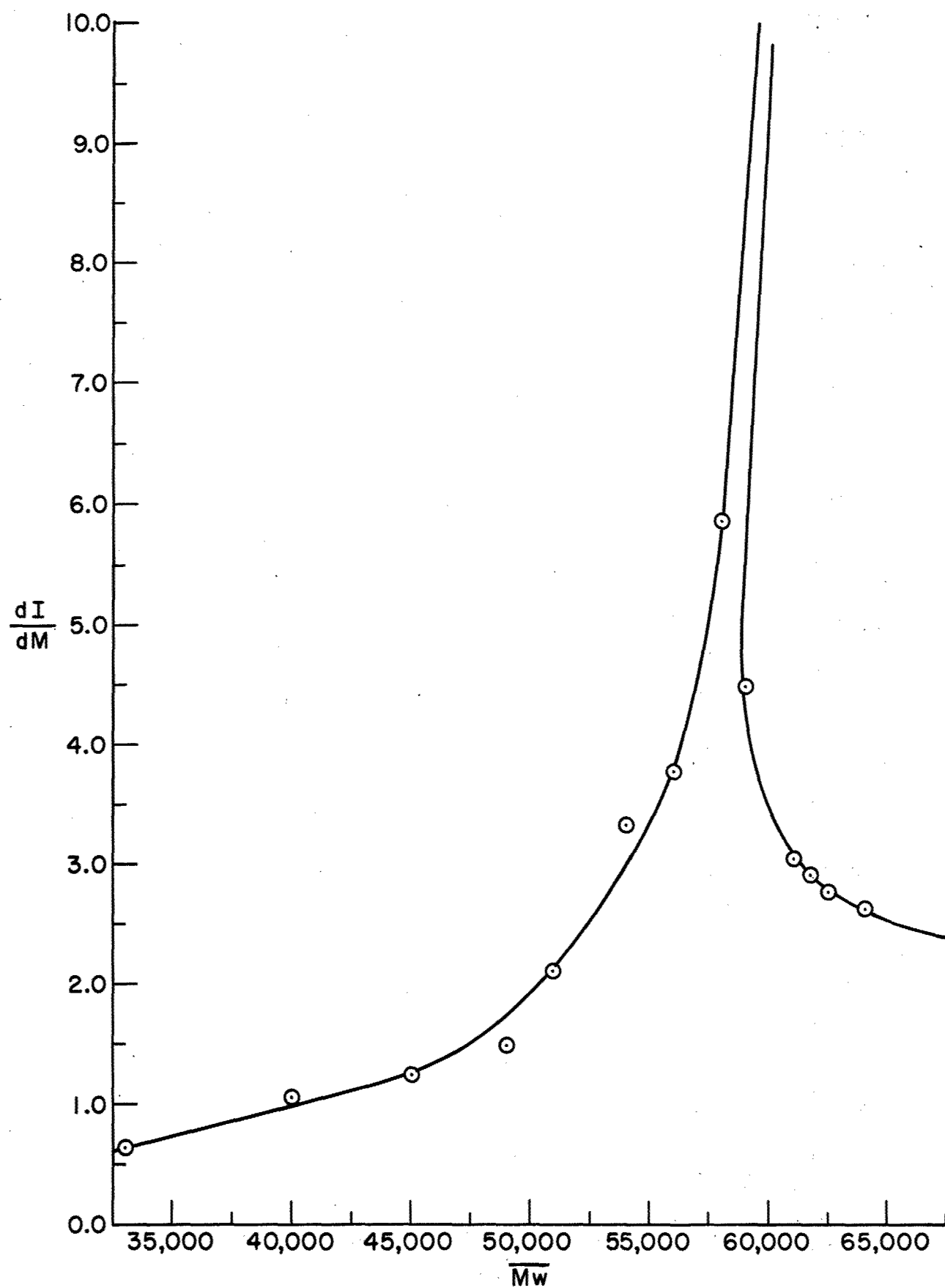


Figure 10. Differential Molecular Weight Distribution Curve for Sample L-XV

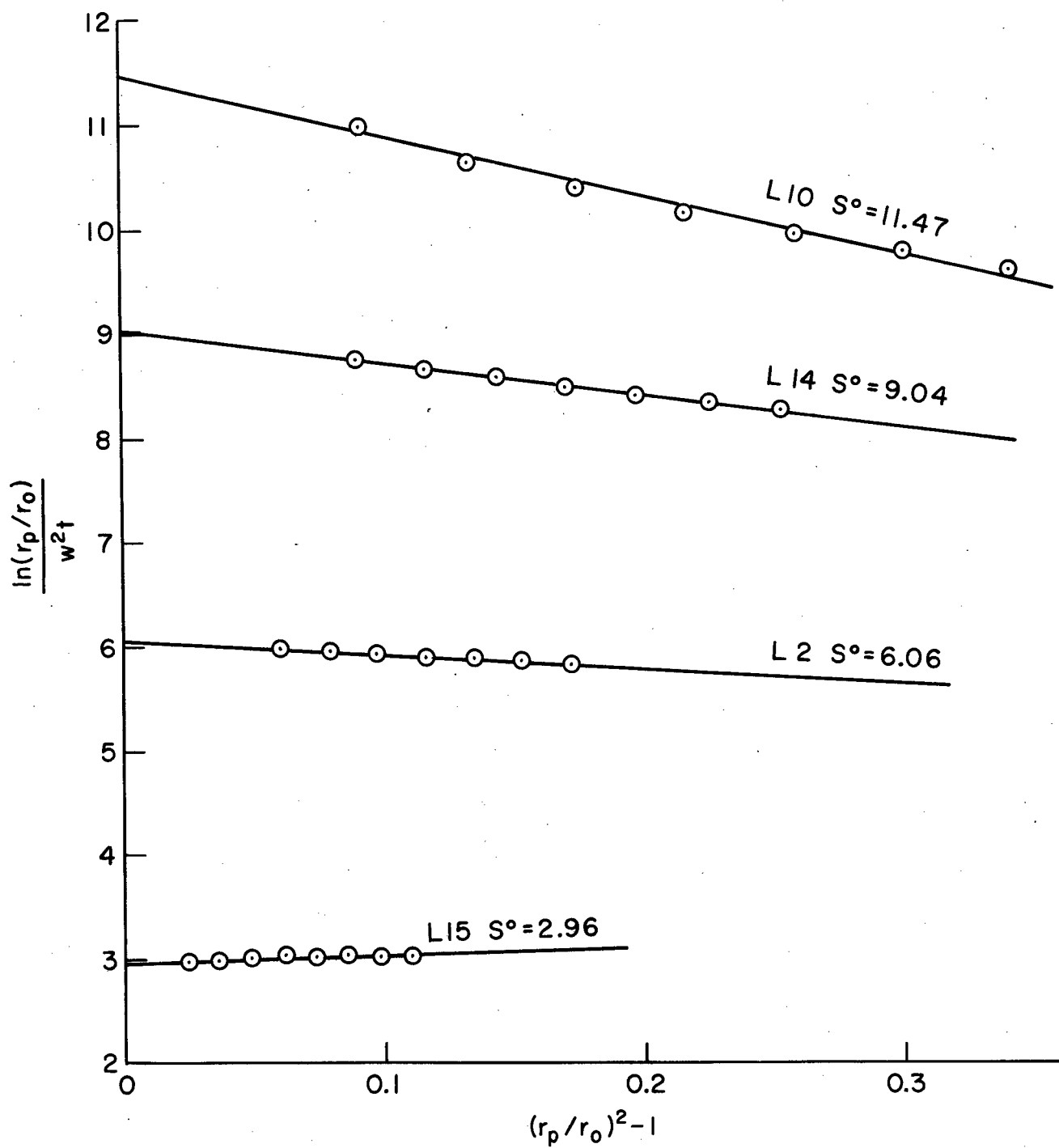
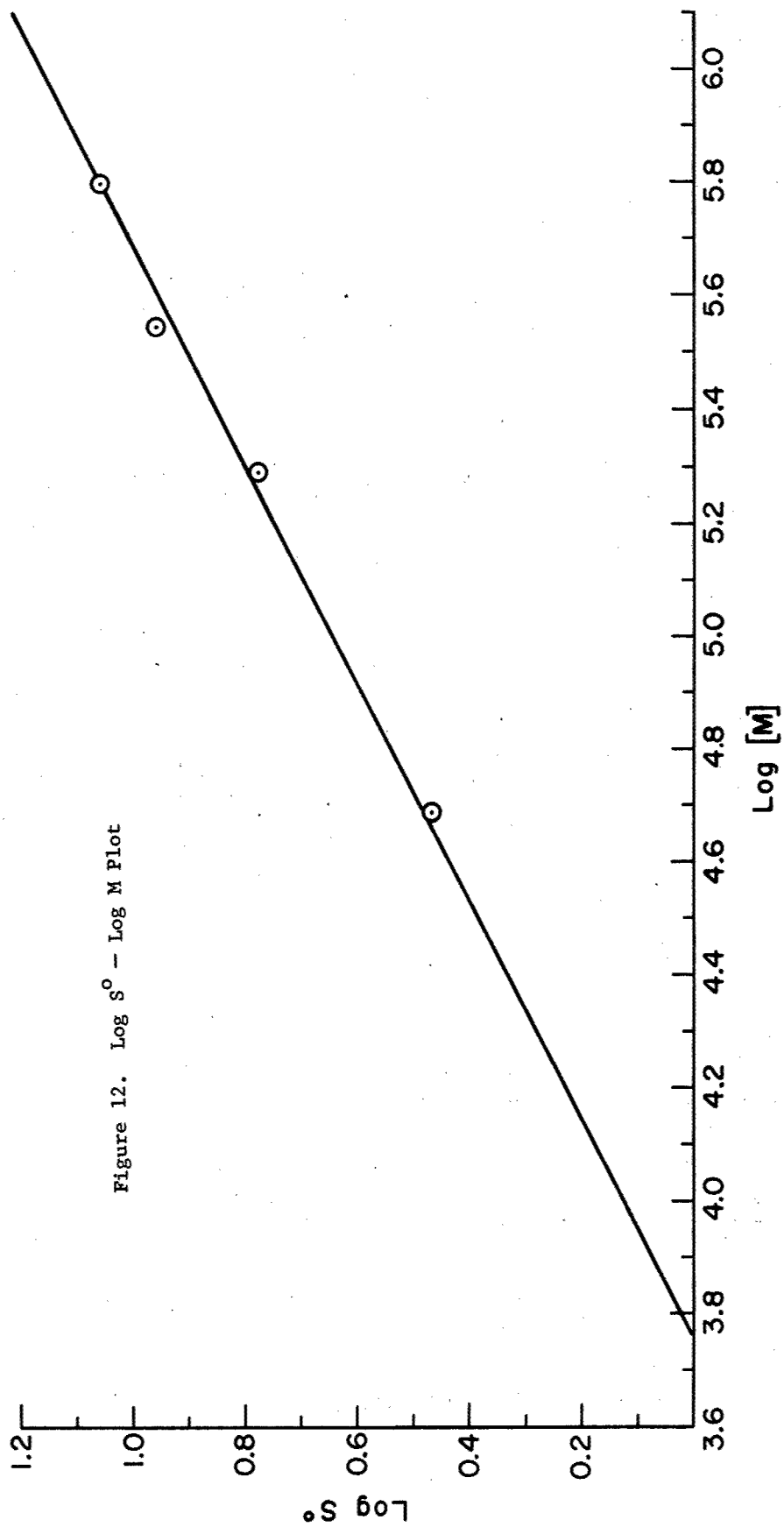


Figure 11. Ultracentrifuge Sedimentation Constants



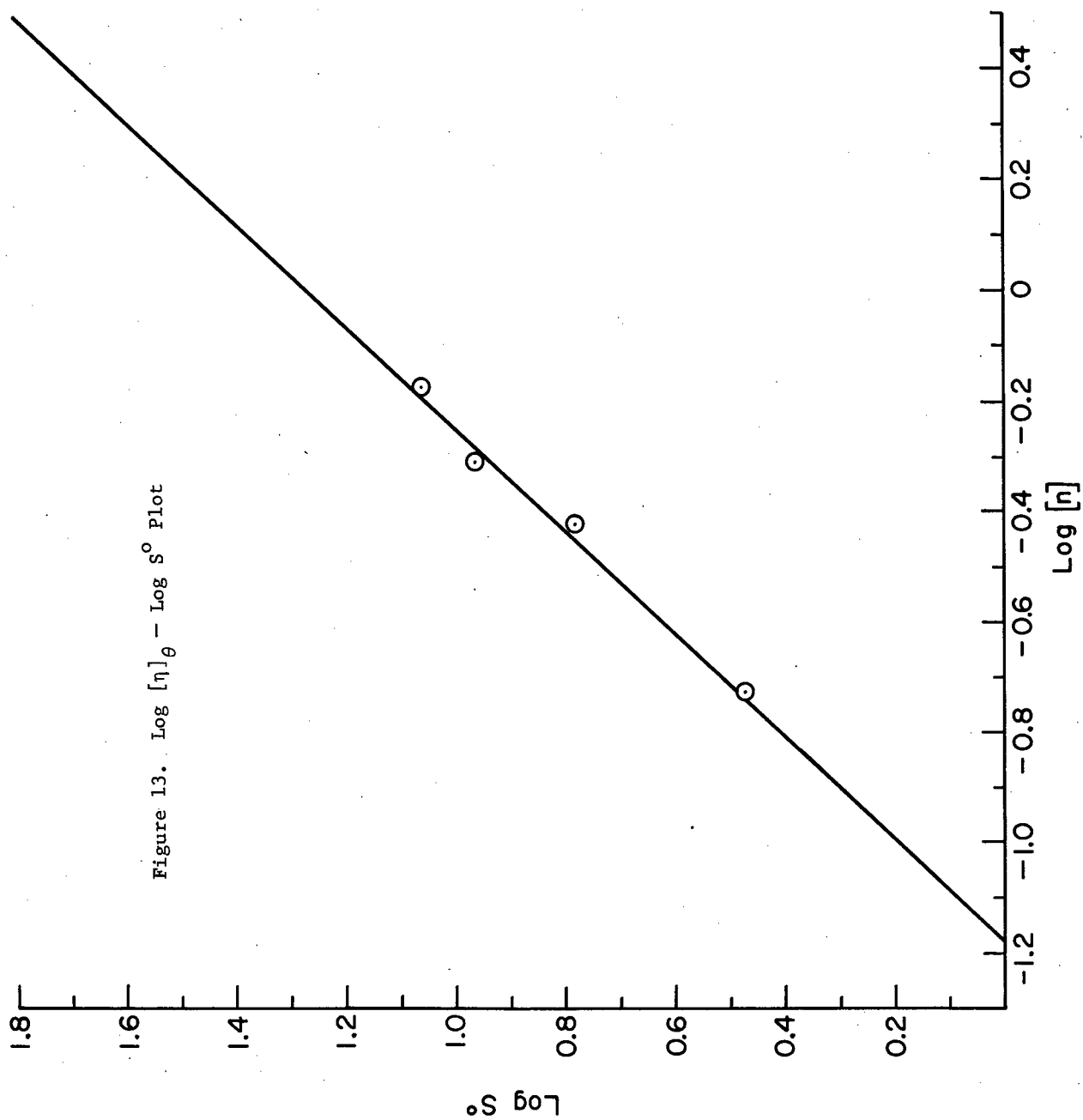
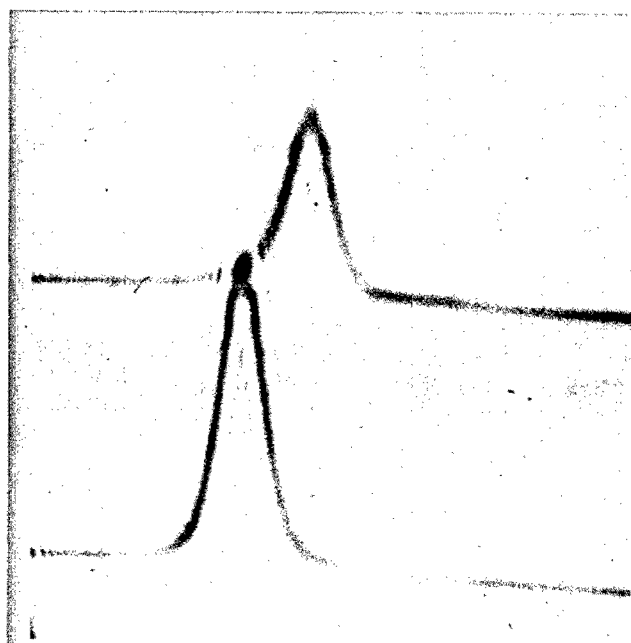
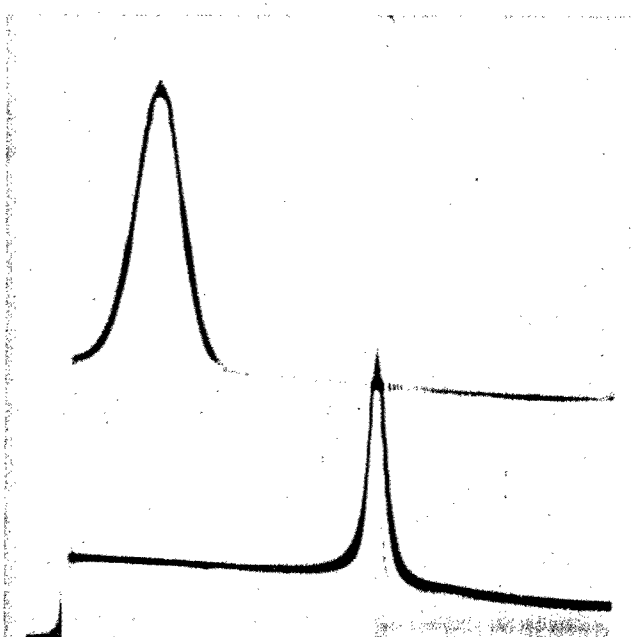


Figure 14. Ultracentrifuge Sedimentation Profiles for Monodisperse Polymers



L-II: upper cell
L-XIV: lower cell



L-XV: upper cell
L-X: lower cell

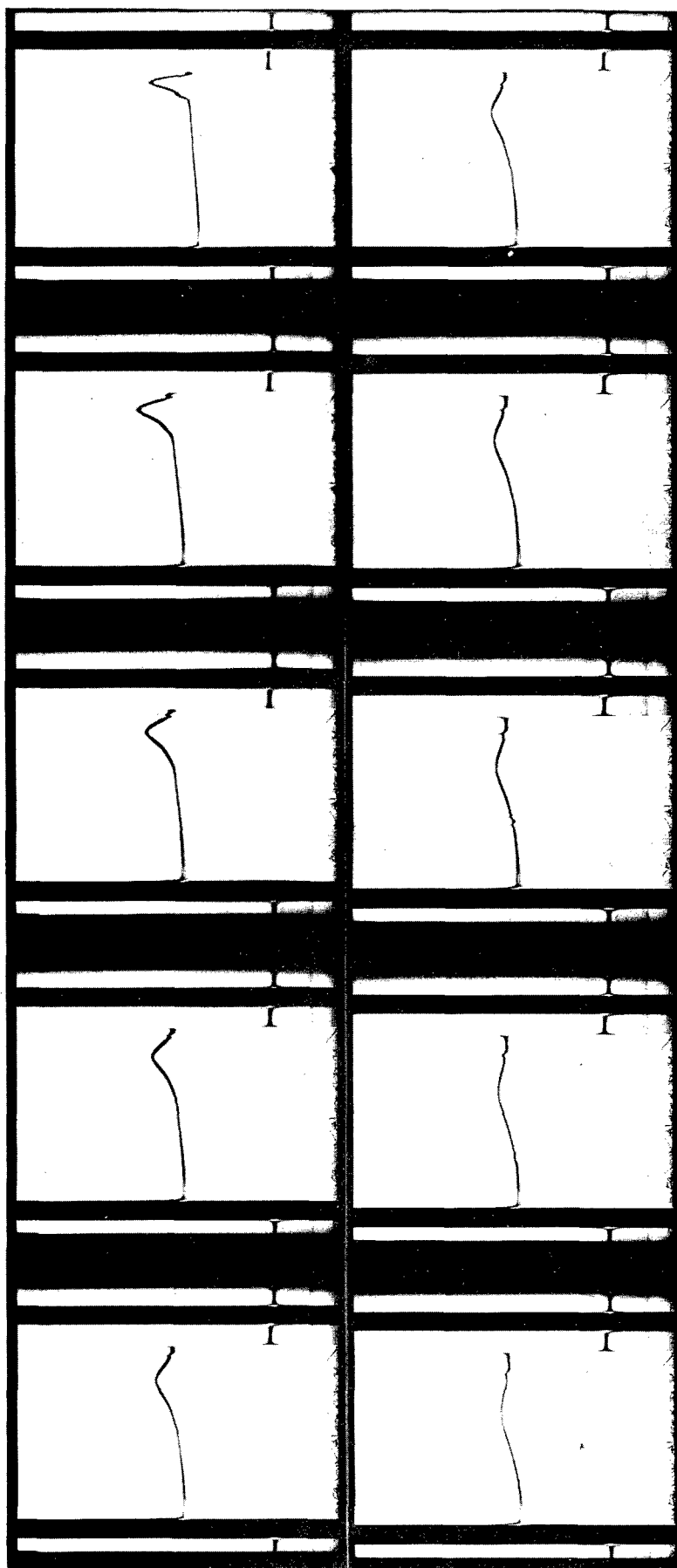


Figure 15. Ultracentrifuge Sedimentation Profiles for a Broad Molecular Weight Distribution Polymer

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Rpt Nr ASD-TDR-62-1110. Final report, Jan 63.
p. incl illus., tables, 24 refs.

Unclassified Report

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scale inert gas reactor for use in the pre-
paration of polystyrene via an anionic poly-
merization is described. The polymers were
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and very narrow molecular weight distri-
butions.

Methods used to characterize and purify

the samples are discussed.

(over)

1. Polystyrene
2. Polymerization
- I. AFSC Project 7340
Task 734004
- II. Contract AF 33
(657) 7651
- III. Mellon Institute,
Pittsburgh, Pa.
- IV. D. F. Wyman,
T. G. Fox
- V. Not aval fr OTS
- VI. In ASTIA collec-
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